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NOVEL DUAL CORES FOR GOLF BALLS

Cross References to Related Applications

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a' ~~This application is a continuation-in-part of~~ U.S. Application Serial No. 08/926,872 filed on September 10, 1997, which is a divisional of U.S. Application Serial No. 08/631,613 filed on April 10, 1996, which in turn is a continuation-in-part of U.S. Application Serial No. 08/591,046 filed on January 25, 1996, and U.S. Application Serial No. 08/542,793 filed on October 13, 1995, which in turn is a continuation-in-part of U.S. Application 08/070,510 filed June 1, 1993. This application is also a continuation-in-part of U.S. Application Serial No. 08/870,585 filed on June 6, 1997, which is a continuation of U.S. Application Serial No. 08/556,237 filed on November 9, 1995, which is a continuation-in-part of U.S. Application Serial No. 08/542,793 filed October 13, 1995, which is a continuation-in-part of U.S. Application Serial No. 08/070,510 filed on June 1, 1993. This application also claims priority on U.S. provisional patent Application ~~Serial No. 60/042,439 filed March 28, 1997.~~

Field of the Invention

The present invention relates to golf balls and, more particularly, to improved gold balls comprising multi-layer covers which have a comparatively hard inner layer and a relatively soft outer layer, and a unique dual core configuration. The improved multi-layer golf balls provide for enhanced distance and durability properties over single layer cover golf balls while at the same time offering enhanced "feel" and spin characteristics generally associated with soft balata and balata-like covers of the prior art.

Background of the Invention

Traditional golf ball covers have been comprised of balata or blends of balata with elastomeric or plastic materials. The traditional balata covers are relatively soft and flexible. Upon impact, the soft balata covers compress against the surface of the club producing high spin. consequently, the soft and flexible balata covers provide an experienced golfer with the ability to apply a spin to control the ball in flight in order to produce a draw or a fade, or a backspin which causes the ball to "bite" or stop abruptly on contact with the green. Moreover, the soft balata covers produce a soft "feel" to the low handicap player. Such playability properties (workability, feel, etc.) are particularly important in short iron play with low swing speeds and are exploited significantly by relatively skilled players.

Despite all the benefits of balata, balata covered golf balls are easily cut and/or damaged if mis-hit. Golf balls produced with balata or balata-containing cover compositions therefore have a relatively short lifespan.

As a result of this negative property, balata and its synthetic substitutes, transpolybutadiene and transpolyisoprene, have been essentially replaced as the cover materials of choice by new cover materials comprising ionomeric resins.

Ionomeric resins are polymers containing interchain ionic bonding. As a result of their toughness, durability and flight characteristics, various ionomeric resins sold by E. I. DuPont de Nemours & Company under the trademark "Surlyn®" and more recently, by the Exxon Corporation (see U.S. Patent No. 4,911,451) under the trademarks "ESCOR®" and the trade name "Iotek," have become the materials of choice for the construction of golf ball covers over the traditional "balata" (transpolyisoprene, natural or

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synthetic) rubbers. As stated, the softer balata covers, although exhibiting enhanced playability properties, lack the durability (cut and abrasion resistance, fatigue endurance, etc.) properties required for repetitive play.

Ionomeric resins are generally ionic copolymers of an olefin, such as ethylene, and a metal salt of an unsaturated carboxylic acid, such as acrylic acid, methacrylic acid, or maleic acid. Metal ions, such as sodium or zinc, are used to neutralize some portion of the acidic group in the copolymer resulting in a thermoplastic elastomer exhibiting enhanced properties, i.e. durability, etc., for golf ball cover construction over balata. However, some of the advantages gained in increased durability have been offset to some degree by the decreases produced in playability. This is because although the ionomeric resins are very durable, they tend to be very hard when utilized for golf ball cover construction, and thus lack the degree of softness required to impart the spin necessary to control the ball in flight. Since the ionomeric resins are harder than balata, the ionomeric resin covers do not compress as much against the face of the club upon impact, thereby producing less spin. In addition, the harder and more durable ionomeric resins lack the "feel" characteristic associated with the softer balata related covers.

As a result, while there are currently more than fifty (50) commercial grades of ionomers available both from DuPont and Exxon, with a wide range of properties which vary according to the type and amount of metal cations, molecular weight, composition of the base resin (i.e., relative content of ethylene and methacrylic and/or acrylic acid groups) and additive ingredients such as reinforcement agents, etc., a great deal of research continues in order to develop a golf ball cover composition exhibiting not only the improved

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impact resistance and carrying distance properties produced by the "hare" ionomeric resins, but also the playability (i.e., "spin," "feel," etc.) characteristics previously associated with the "soft" balata covers, properties which are still desired by the more skilled golfer.

Consequently, a number of two-piece (a solid resilient center or core with a molded cover) and three-piece (a liquid or solid center, elastomeric winding about the center, and a molded cover) golf balls have been produced to address these needs. the different types of materials utilized to formulate the cores, coves, etc. of these balls dramatically alters the balls' overall characteristics. In addition, multi-layered covers containing one or more ionomer resins have also been formulated in an attempt to produce a golf ball having the overall distance, playability and durability characteristics desired.

This was addressed by Spalding & Evenflo Companies, Inc., the assignee of the present invention, in U.S. Patent No. 4,431,193 where a multi-layered golf ball is produced by initially molding a first cover layer on a spherical core and then adding a second layer. The first layer is comprised of a hard, high flexural modulus resinous material such as type 1605 Surlyn® (now designated Surlyn® 8940). type 1605 Surlyn (Surlyn® 8940) is a sodium ion based low acid (less than or equal to 15 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 51,000 psi. An outer layer of a comparatively soft, low flexural modulus resinous material such as type 1855 Surlyn® (now designated Surlyn® 9020) is molded over the inner cover layer. Type 1855 Surlyn® (Surlyn® 9020) is a zinc ion based low acid (10 weight percent methacrylic acid) ionomer resin having a flexural modulus of about 14,000 psi.

The '193 patent teaches that the hard, high flexural modulus resin which comprises the first layer provides for a gain in coefficient of restitution over the coefficient of restitution of the core. The increase in the coefficient of restitution provides a ball which serves to attain or approach the maximum initial velocity limit of 255 feet per second as provided by the United States Golf Association (U.S.G.A.) rules. The relatively soft, low flexural modulus outer layer provides for the advantageous "feel" and playing characteristics of a balata covered golf ball.

In various attempts to produce a durable, high spin ionomer golf ball, the golfing industry has blended the hard ionomer resins with a number of softer ionomeric resins. U.S. Patent Nos. 4884,814 and 5,120,791 are directed to cover compositions containing blends of hard and soft ionomeric resins. The hard copolymers typically are made from an olefin and an unsaturated carboxylic acid. The soft copolymers are generally made from an olefin, an unsaturated carboxylic acid, and an acrylate ester. It has been found that golf ball covers formed from hard=soft ionomer blends tend to become scuffed more readily than covers made of hard ionomer alone. It would be useful to develop a golf ball having a combination of softness and durability which is better than the softness-durability combination of a golf ball cover made from a hard-soft ionomer blend.

Most professional golfers and good amateur golfers desire a golf ball that provides distance when hit off a driver, control and stopping ability on full iron shots, and high spin on short "touch and feel" shots. Many conventional two-piece and thread wound performance golf balls have undesirable high spin rates on full shots. The excessive spin on full shots is a sacrifice made in order to achieve more spin which is

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desired on the shorter touch shots. It would be beneficial to provide a golf ball which has high spin for touch shots without generating excessive spin or full shots.

These and other objects and features of the invention will be apparent from the following summary and description of the invention, the drawings and from the claims.

Summary of the Invention

In one aspect, the present invention provides a golf ball comprising a dual core comprising a center component and a core layer disposed about the center component. The golf ball further comprises an inner cover layer molded on the inner cover layer. The inner cover layer is formed from a high acid ionomer including at least 16% by weight of an alpha, beta-unsaturated carboxylic acid. The outer cover layer is formed from a relatively soft polymeric material such as low flexural modulus ionomer resins and non-ionomeric thermoplastic elastomers.

In yet another aspect, the present invention provides a multi-layer golf ball comprising a dual core component that includes an interior spherical center component and a core layer disposed about the spherical center component. The golf ball further comprises an inner cover layer molded over the core layer of the dual core, and an outer cover layer molded over the inner cover layer. The inner and outer cover layers have particular properties. The inner cover layer comprises an ionomeric resin including at least 16% by weight of an alpha, beta-unsaturated carboxylic acid and has a modulus of from about 15,000 to about 70,000 psi. The outer cover layer comprises a blend of a sodium or zinc salt of a particular copolymer and a particular unsaturated monocarboxylic acid, and a sodium or zinc salt of a certain terpolymer, acrylic acid and a

particular unsaturated monomer of the acrylate ester class. The outer cover layer has a modulus of from about 1,000 to about 30,000 psi.

In yet another embodiment, the present invention provides a multi-layer golf ball comprising a spherical dual core, an inner cover layer molded over the dual core, and an outer cover layer molded over the inner cover layer. The inner cover layer comprises an ionomeric resin including 17% to 25% of an alpha, beta-unsaturated carboxylic acid, and has a modulus of from about 15,000 to about 70,000 psi. The outer cover layer comprises a non-ionomeric thermoplastic selected from the group consisting of polyester elastomer, polyester urethane, and polyester amide. The outer cover layer has a modulus in the range of 1,000 to 30,000 psi.

In a further aspect, the present invention also provides a golf ball comprising a dual core, an inner cover layer molded on the dual core, an outer cover layer molded on the inner cover layer, and at least one outer core layer disposed about the dual core. The inner cover layer comprises a high acid ionomer including at least 16% of an alpha, beta-unsaturated carboxylic acid. The outer cover layer comprises a relatively soft polymeric material of low flexural modulus ionomer resins and non-ionomeric thermoplastic elastomers.

In yet another aspect, the present invention provides a multi-layer golf ball comprising a spherical dual core including an interior spherical center and a core layer disposed about the center. The golf ball further comprises an inner cover layer molded over the spherical dual core, an outer cover layer molded over the inner cover layer, and at least one inner core layer disposed between the dual core and the inner cover layer. The inner cover layer comprises an ionomeric resin including at least 16% of an alpha, beta-unsaturated carboxylic acid, and has a modulus of from

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15,000 to 70,000 psi. The outer cover layer comprises a particular blend of a sodium or zinc salt of a certain copolymer and a sodium or zinc salt of a terpolymer. The outer cover layer has a modulus of 1,000 to 30,000 psi.

Moreover, the present invention provides a multi-layer golf ball comprising a dual core component, an inner cover molded over the dual core, an outer core layer molded over the inner cover, and at least one outer core layer disposed between the dual core and the inner cover layer. The inner cover layer comprises an ionomeric resin including 17% to 25% of an alpha, beta-unsaturated carboxylic acid and has a modulus of 15,000 to 70,000 psi. The outer cover layer comprises a non-ionomeric thermoplastic of a polyester elastomer, a polyester polyurethane and a polyester amide. The outer cover has a modulus in the range of 1,000 to 3,000 psi.

Brief Description of the Drawings

FIGURE 1 is a cross-sectional view of a preferred embodiment golf ball in accordance with the present invention illustrating a core and a cover comprising an inner layer and an outer dimpled layer;

FIGURE 2 is a diametrical cross-sectional view of the preferred embodiment golf ball depicted in FIGURE 1 having a core and a cover comprising an inner layer surrounding the core and an outer layer having a plurality of dimples;

FIGURE 3 is a cross-sectional view of another preferred embodiment golf ball in accordance with the present invention comprising a dual core component;

FIGURE 4 is a cross-sectional view of yet another preferred embodiment golf ball in accordance with the present invention comprising a dual core component;

FIGURE 5 is a cross-sectional view of another preferred embodiment golf ball in accordance with the present invention

present invention comprising a dual core component and an outer cover layer;

FIGURE 6 is a cross-sectional view of yet another preferred embodiment golf ball in accordance with the present invention comprising a dual core component and an outer core layer; and

FIGURE 7 is a schematic view of an assembly used for molding a preferred embodiment golf ball in accordance with the present invention.

Detailed Description of the Preferred Embodiments

The present invention is directed to a golf ball comprising a dual-core component and a multi-layer cover. The novel multi-layer golf ball covers of the present invention include a first or inner layer or ply of a high acid (greater than 16 weight percent acid) ionomer blend or, more preferably, a low acid (16 weight percent acid or less) ionomer blend and second or outer layer or ply comprised of a comparatively softer, low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic or thermosetting elastomer such as polyurethane or polyester elastomer. The multi-layer golf balls of the present invention can be of standard or enlarged size. Preferably, the inner layer or ply includes a blend of low acid ionomers and has a Shore D hardness of 70 or greater and the outer cover layer comprised of polyurethane and has a Shore D hardness of about 45 (i.e., Shore C hardness of about 65).

The present invention golf balls utilize a unique dual-core configuration. Preferably, the cores comprise (i) an interior spherical center component formed from a thermoset material, a thermoplastic material, or combinations thereof; and (ii) a core layer disposed about the spherical center component, the core layer formed from a thermoset material, a thermoplastic material, or combinations thereof. The cores may

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further comprise (iii) an optional outer core layer disposed about the core layer. The outer core layer may be formed from a thermoset material, a thermoplastic material, or combinations thereof.

Although the present invention is primarily directed to golf balls comprising a dual core component and a multi-layer cover as described herein, the present invention also includes golf balls having a dual core component and conventional covers comprising balata, various thermoplastic materials, cast polyurethanes, or any other known cover materials.

It has been found that multi-layer golf balls having inner and outer cover layers exhibit higher C.O.R. values and have greater travel distance in comparison with balls made from a single cover layer. In addition, it has been found that use of an inner cover layer constructed of a blend of low acid (i.e., 16 weight percent acid or less) ionomer resins produces softer compression and higher spin rates than inner cover layers constructed of high acid ionomer resins. This is compounded by the fact that the softer polyurethane outer layer adds to the desirable "feel" and high spin rate while maintaining respectable resilience. The soft outer layer allows the cover to deform more during impact and increases the area of contact between the club face and the cover, thereby imparting more spin on the ball. As a result, the soft polyurethane cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability.

Consequently, the overall combination of the unique dual core configuration, described in greater detail herein, and the multi-layer cover construction of inner and outer cover layers made, for example, from blends of low acid ionomer resins and polyurethane results in a standard size or oversized golf ball having enhanced resilience (improved travel distance) and

durability (i.e. cut resistance, etc.) characteristics while maintaining and in many instances, improving the ball's playability properties.

The combination of a low acid ionomer blend inner cover layer with a soft, relatively low modulus ionomer, polyurethane based elastomer outer cover layer provides for good overall coefficient of restitution (i.e., enhanced resilience) while at the same time demonstrating improved compression and spin. The outer cover layer generally contributes to a more desirable feel and spin, particularly at lower swing speeds with highly lofted clubs such as half wedge shots.

Accordingly, the present invention is directed to a golf ball comprising a dual-core configuration and an improved multi-layer cover which produces, upon molding each layer around a core to formulate a multi-layer cover, a golf ball exhibiting enhanced distance (i.e., resilience) without adversely affecting, and in many instances, improving the ball's playability (hardness/softness) and/or durability (i.e., cut resistance, fatigue resistance, etc.) characteristics.

Figures 1 and 2 illustrate a preferred embodiment golf ball 5 in accordance with the present invention. It will be understood that none of the referenced figures are to scale. And so, the thicknesses and proportions of the various layers and the diameter of the various core components are not necessarily as depicted. The golf ball 5 comprises a multi-layered cover 12 disposed about a core 10. The core 10 of the golf ball can be formed of a solid, a liquid, or any other substances that may be utilized to form the novel dual core described herein. The multi-layered cover 12 comprises two layers: a first or inner layer or ply 14 and a second or outer layer or ply 16. The inner layer 14 can be ionomer, ionomer blends, non-ionomer, non-ionomer blends, or blends of ionomer and non-ionomer. The outer layer 16 is softer than the

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inner layer and can be ionomer, ionomer blends, non-ionomer, non-ionomer blends or blends of ionomer and non-ionomer.

In a first preferred embodiment, the inner layer 14 is comprised of a high acid (i.e. greater than 16 weight percent acid) ionomer resin or high acid ionomer blend. Preferably, the inner layer is comprised of a blend of two or more high acid (i.e., at least 16 weight percent acid) ionomer resins neutralized to various extents by different metal cations. The inner cover layer may or may not include a metal stearate (e.g., zinc stearate) or other metal fatty acid salt. The purpose of the metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball. In a second embodiment, the inner layer 14 is comprised of a low acid (i.e., 16 weight percent acid or less) ionomer blend. Preferably, the inner layer is comprised of a blend of two or more low acid (i.e., 16 weight percent acid or less) ionomer resins neutralized to various extents by different metal cations. The inner cover layer may or may not include a metal stearate (e.g., zinc stearate) or other metal fatty acid salt. The purpose of the metal stearate or other metal fatty acid salt is to lower the cost of production without affecting the overall performance of the finished golf ball.

Two principal properties involved in golf ball performance are resilience and hardness. Resilience is determined by the coefficient of restitution (C.O.R.), the constant "e" which is the ratio of the relative velocity of two elastic spheres after direct impact to that before impact. As a result, the coefficient of restitution ("e") can vary from 0 to 1, with 1 being equivalent to an elastic collision and 0 being equivalent to an inelastic collision.

Resilience (C.O.R.), along with additional factors such as club head speed, angle of trajectory and ball configuration (i.e., dimple pattern) generally determine the distance a ball will travel when hit. Since club head speed and the angle of trajectory are factors not easily controllable by a manufacturer, factors of concern among manufacturers are the coefficient of restitution (C.O.R.) and the surface configuration of the ball.

The coefficient of restitution (C.O.R.) in solid core balls is a function of the composition of the molded core and of the cover. In balls containing a dual core (i.e., balls comprising an interior spherical center component, a core layer disposed about the spherical center component, and a cover), the coefficient of restitution is a function of not only the composition of the cover, but also the composition and physical characteristics of the interior spherical center component and core layer. Both the dual core and the cover contribute to the coefficient of restitution in the golf balls of the present invention.

In this regard, the coefficient of restitution of a golf ball is generally measured by propelling a ball at a given speed against a hard surface and measuring the ball's incoming and outgoing velocity electronically. As mentioned above, the coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. The coefficient of restitution must be carefully controlled in all commercial golf balls in order for the ball to be within the specifications regulated by the United States Golf Association (U.S.G.A.) Along this line, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity (i.e., the speed off the club) exceeding 255 feet per second. Since the coefficient of restitution of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having

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sufficiently high coefficient of restitution to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

The hardness of the ball is the second principal property involved in the performance of a golf ball. The hardness of the ball can affect the playability of the ball on striking and the sound or "click" produced. Hardness is determined by the deformation (i.e., compression) of the ball under various load conditions applied across the ball's diameter (i.e., the lower the compression value, the harder the material). As indicated in U.S. Patent No. 4,674,751, softer covers permit the accomplished golfer to impart proper spin. This is because the softer covers deform on impact significantly more than balls having "harder" ionomeric resin covers. As a result, the better player is allowed to impart fade, draw or backspin to the ball thereby enhancing playability. Such properties may be determined by various spin rate tests.

It has been found that a hard inner layer provides for a substantial increase in resilience (i.e., enhanced distance) over known multi-layer covered balls. The softer outer layer provides for desirable "feel" and high spin rate while maintaining respectable resiliency. The soft outer layer allows the cover to deform more during impact and increases the area of contact between the club face and the cover, thereby imparting more spin on the ball. As a result, the soft cover provides the ball with a balata-like feel and playability characteristics with improved distance and durability. Consequently, the overall combination of the inner and outer cover layers results in a golf ball having enhanced resilience (improved travel distance) and durability (i.e., cut resistance, etc.) characteristics

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while maintaining and in many instances, improving the playability properties of the ball.

The combination of a hard inner cover layer with a soft, relatively low modulus ionomer, ionomer blend or other non-ionomeric thermoplastic elastomer outer cover layer provides for excellent overall coefficient of restitution (i.e., excellent resilience) because of the improved resiliency produced by the inner cover layer. While some improvement in resiliency is also produced by the outer cover layer, the outer cover layer generally provides for a more desirable feel and high spin, particularly at lower swing speeds with highly lofted clubs such as half wedge shots.

Inner Cover Layer

The inner cover layer is harder than the outer cover layer and generally has a thickness in the range of 0.01 to 0.10 inches, preferably 0.03 to 0.07 inches for a 1.68 inch ball and 0.05 to 0.10 inches for a 1.72 inch (or more) ball. The core and inner cover layer together form an inner ball having a coefficient of restitution of 0.780 or more and more preferably 0.790 or more, and a diameter in the range of 1.48 - 1.66 inches for a 1.68 inch ball and 1.50 - 1.70 inches for a 1.72 inch (or more) ball. The inner cover layer has a Shore D hardness of 60 or more. It is particularly advantageous if the golf balls of the invention have an inner layer with a Shore D hardness of 65 or more. The above-described characteristics of the inner cover layer provide an inner ball having a PGA compression of 100 or less. It is found that when the inner ball has a PGA compression of 90 or less, excellent playability results.

The inner layer compositions include the high acid ionomers such as those developed by E.I. DuPont de Nemours & Company under the trademark "Surlyn®" and by Exxon Corporation under the trademark "Escor®" or trade

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name "Iotek", or blends thereof. Examples of compositions which may be used as the inner layer herein are set forth in detail in a continuation of U.S. Application Serial No. 08/174,765, now abandoned, which is a continuation of U.S. Application Serial No. 07/776,803 filed October 15, 1991, now abandoned, and Serial No. 08/493,089, a2 which is a continuation of 07/981,751, now abandoned, which in turn is a continuation of Serial No. 07/901,660 filed June 19, 1992, now abandoned, all of which are incorporated herein by reference. Of course, the inner layer high acid ionomer compositions are not limited in any way to those compositions set forth in said applications.

The high acid ionomers which may be suitable for use in formulating the inner layer compositions are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10-100%, preferably 30-70%) by the metal ions. Each of the high acid ionomer resins which may be included in the inner layer cover compositions of the invention contains greater than about 16% by weight of a carboxylic acid, preferably from about 17% to about 25% by weight of a carboxylic acid, more preferably from about 18.5% to about 21.5% by weight of a carboxylic acid.

Although the inner layer cover composition of several embodiments of the present invention preferably includes a high acid ionomeric resin, the scope of the patent embraces all known high acid ionomeric resins

falling within the parameters set forth above, only a relatively limited number of these high acid ionomeric resins have recently become commercially available.

The high acid ionomeric resins available from Exxon under the designation "Escor®" and or "Iotek", are somewhat similar to the high acid ionomeric resins available under the "Surlyn®" trademark. However, since the Escor®/Iotek ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the "Surlyn®" resins are zinc, sodium, magnesium, etc. salts of poly(ethylene-methacrylic acid), distinct differences in properties exist.

Examples of the high acid methacrylic acid based ionomers found suitable for use in accordance with this invention include Surlyn®8220 and 8240 (both formerly known as forms of Surlyn AD-8422), Surlyn®9220 (zinc cation), Surlyn®SEP-503-1 (zinc cation), and Surlyn®SEP-503-2 (magnesium cation). According to DuPont, all of these ionomers contain from about 18.5 to about 21.5% by weight methacrylic acid.

More particularly, Surlyn® AD-8422 is currently commercially available from DuPont in a number of different grades (i.e., AD-8422-2, AD-8422-3, AD-8422-5, etc.) based upon differences in melt index. According to DuPont, Surlyn® 8422, which is believed recently to have been redesignated as 8220 and 8240, offers the following general properties when compared to Surlyn® 8920, the stiffest, hardest of all on the low acid grades (referred to as "hard" ionomers in U.S. Patent No. 4,884,814):

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T190X

	LOW ACID (15 wt% Acid)	HIGH ACID (>20 wt% Acid)	
	SURLYN® 8920	SURLYN® 8422-2	SURLYN® 8422-3
IONOMER			
Cation	Na	Na	Na
Melt Index	1.2	2.8	1.0
Sodium, Wt%	2.3	1.9	2.4
Base Resin MI	60	60	60
MP[1], °C	88	86	85
FP[1], °C	47	48.5	45
COMPRESSION MOLDING[2]			
Tensile Break, psi	4350	4190	5330
Yield, psi	2880	3670	3590
Elongation, %	315	263	289
Flex Mod, K psi	53.2	76.4	88.3
Shore D hardness	66	67	68

[1] DSC second heat, 10°C/min heating rate.
[2] Samples compression molded at 150°C annealed 24 hours at 60°C. 8422-2, -3 were homogenized at 190°C before molding.

In comparing Surlyn® 8920 to Surlyn® 8422-2 and Surlyn® 8422-3, it is noted that the high acid Surlyn® 8422-2 and 8422-3 ionomers have a higher tensile yield, lower elongation, slightly higher Shore D hardness and much higher flexural modulus. Surlyn® 8920 contains 15 weight percent methacrylic acid and is 59% neutralized with sodium.

In addition, Surlyn®SEP-503-1 (zinc cation) and Surlyn®SEP-503-2 (magnesium cation) are high acid zinc and magnesium versions of the Surlyn®AD 8422 high acid ionomers. When compared to the Surlyn® AD 8422 high acid ionomers, the Surlyn® SEP-503-1 and SEP-503-2 ionomers can be defined as follows:

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T200X

Surlyn® Ionomer	Ion	Melt Index	Neutralization %
AD 8422-3	Na	1.0	45
SEP 503-1	Zn	0.8	38
SEP 503-2	Mg	1.8	43

Further, Surlyn® 8162 is a zinc cation ionomer resin containing approximately 20% by weight (i.e., 18.5 - 21.5% weight) methacrylic acid copolymer that has been 30 - 70% neutralized. Surlyn® 8162 is currently commercially available from DuPont.

Examples of the high acid acrylic acid based ionomers suitable for use in the present invention also include the Escor® or Iotek high acid ethylene acrylic acid ionomers produced by Exxon such as Ex 1001, 1002, 959, 960, 989, 990, 1003, 1004, 993, 994. In this regard, Escor® or Iotek 959 is a sodium ion neutralized ethylene-acrylic neutralized ethylene-acrylic acid copolymer. According to Exxon, Ioteks 959 and 960 contain from about 19.0 to 21.0% by weight acrylic acid with approximately 30 to about 70 percent of the acid groups neutralized with sodium and zinc ions, respectively. The physical properties of these high acid acrylic acid based ionomers are set forth in Tables 1 and 2 as follows:

T210X

TABLE 1

Physical Properties of Various Ionomers

PROPERTY	Ex1001	Ex1002	ESCOR® (IOTEK) 959	Ex1003	Ex1004	ESCOR® (IOTEK) 960
Melt index, g/10 min	1.0	1.6	2.0	1.1	2.0	1.8
Cation	Na	Na	Na	Zn	Zn	Zn
Melting Point, °F	183	183	172	180	180.5	174
Vicat Softening Point, °F	125	125	130	133	131	131
Tensile @ Break	34.4 MPa	22.5 MPa	4600 psi	24.8 MPa	20.6 MPa	3500 psi
Elongation @ Break, %	341	348	325	387	437	430
Hardness, Shore D	63	62	66	54	53	57
Flexural Modulus	365 MPa	380 MPa	66,000 psi	147 MPa	130 MPa	27,000 psi

TABLE 2

Physical Properties of Various Ionomers

T211X

		EX 989	EX 993	EX 994	EX 990
Melt index	g/10 min	1.30	1.25	1.32	1.24
Moisture	ppm	482	214	997	654
Cation type	-	Na	Li	K	Zn
M+ content by AAS	wt%	2.74	0.87	4.54	0
Zn content by AAS	wt%	0	0	0	3.16
Density	kg/m³	959	945	976	977
Vicat softening point	°C	52.5	51	50	55.0
Crystallization point	°C	40.1	39.8	44.9	54.4
Melting point	°C	82.6	81.0	80.4	81.0
Tensile at yield	MPa	23.8	24.6	22	16.5
Tensile at break	MPa	32.3	31.1	29.7	23.8
Elongation at break	%	330	260	340	357
1% secant modulus	MPa	389	379	312	205
Flexural modulus	MPa	340	368	303	183
Abrasion resistance	mg	20.0	9.2	15.2	20.5
Hardness Shore D	-	62	62.5	61	56
Zwick Rebound	%	61	63	59	48

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Furthermore, as a result of the development by the assignee of this application of a number of new high acid ionomers neutralized to various extents by several different types of metal cations, such as by manganese, lithium, potassium, calcium and nickel cations, several new high acid ionomers and/or high acid ionomer blends besides sodium, zinc and magnesium high acid ionomers or ionomer blends are now available for golf ball cover production. It has been found that these new cation neutralized high acid ionomer blends produce inner cover layer compositions exhibiting enhanced hardness and resilience due to synergies which occur during processing. Consequently, the metal cation neutralized high acid ionomer resins recently produced can be blended to produce substantially higher C.O.R.'s than those produced by the low acid ionomer inner cover compositions presently commercially available.

More particularly, several new metal cation neutralized high acid ionomer resins have been produced by the inventor by neutralizing, to various extends, high acid copolymers of an alpha-olefin and an alpha, beta-unsaturated carboxylic acid with a wide variety of different metal cation salts. This discovery is the subject matter of U.S. Application Serial No. Ins a3 08/493,089, a3 incorporated herein by reference. It has been found that numerous new metal cation neutralized high acid ionomer resins can be obtained by reacting a high acid copolymer (i.e., a copolymer containing greater than 16% by weight acid, preferably from about 17 to about 25 weight percent acid, and more preferably about 20 weight percent acid), with a metal cation salt capable of ionizing or neutralizing the copolymer to the extent desired (i.e., from about 10% to 90%).

The base copolymer is made up of greater than 16% by weight of an alpha, beta-unsaturated carboxylic acid and an alpha-olefin. Optionally, a softening comonomer can be included in the copolymer. Generally,

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the alpha-olefin has from 2 to 10 carbon atoms and is preferably ethylene, and the unsaturated carboxylic acid is a carboxylic acid having from about 3 to 8 carbons. Examples of such acids include acrylic acid, methacrylic acid, ethacrylic acid, chloroacrylic acid, crotonic acid, maleic acid, fumaric acid, and itaconic acid, with acrylic acid being preferred.

The softening comonomer that can be optionally included in the inner cover layer for the golf ball of the invention may be selected from the group consisting of vinyl esters of aliphatic carboxylic acids wherein the acids have 2 to 10 carb/n atoms, vinyl ethers wherein the alkyl groups contains 1 to 10 carbon atoms, and alkyl acrylates or methacrylates wherein the alkyl group contains 1 to 10 carbon atoms. Suitable softening comonomers include vinyl acetate, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, or the like.

Consequently, examples of a number of copolymers suitable for use to produce the high acid ionomers included in the present invention include, but are not limited to, high acid embodiments of an ethylene/acrylic acid copolymer, an ethylene/methacrylic acid copolymer, an ethylene/itaconic acid copolymer, an ethylene/maleic acid copolymer, an ethylene/methacrylic acid/vinyl acetate copolymer, an ethylene/acrylic acid/vinyl alcohol copolymer, etc. The base copolymer broadly contains greater than 16% by weight unsaturated carboxylic acid, from about 39 to about 83% by weight ethylene and from 0 to about 40% by weight of a softening comonomer. Preferably, the copolymer contains about 20% by weight unsaturated carboxylic acid and about 80% by weight ethylene. Most preferably, the copolymer contains about 20% acrylic acid with the remainder being ethylene.

Along these lines, examples of the preferred high acid base copolymers which fulfill the criteria set

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forth above, are a series of ethylene-acrylic copolymers which are commercially available from The Dow Chemical Company, Midland, Michigan, under the "Primacor" designation. These high acid base copolymers exhibit the typical properties set forth below in Table 3.

T240X

TABLE 3

Typical Properties of Primacor Ethylene-Acrylic Acid Copolymers

GRADE	PERCENT ACID	DENSITY, glcc	MELT INDEX, g/10min	TENSILE YD. ST (psi)	FLEXURAL MODULUS (psi)	VICAT SOFT PT (°C)	SHORE D HARDNESS
ASTM		D-792	D-1238	D-638	D-790	D-1525	D-2240
5980	20.0	0.958	300.0	-	4800	43	50
5990	20.0	0.955	1300.0	650	2600	40	42
5990	20.0	0.955	1300.0	650	3200	40	42
5981	20.0	0.960	300.0	900	3200	46	48
5981	20.0	0.960	300.0	900	3200	46	48
5983	20.0	0.958	500.0	850	3100	44	45
5991	20.0	0.953	2600.0	635	2600	38	40

[1]The Melt Index values are obtained according to ASTM D-1238, at 190°C.

Due to the high molecular weight of the Primacor 5981 grade of the ethylene-acrylic acid copolymer, this copolymer is the more preferred grade utilized in the invention.

The metal cation salts utilized in the invention are those salts which provide the metal cations capable of neutralizing, to various extents, the carboxylic acid groups of the high acid copolymer. These include acetate, oxide or hydroxide salts of lithium, calcium, zinc, sodium, potassium, nickel, magnesium, and manganese.

Examples of such lithium ion sources are lithium hydroxide monohydrate, lithium hydroxide, lithium oxide and lithium acetate. Sources for the calcium ion include calcium hydroxide, calcium acetate and calcium oxide. suitable zinc ion sources are zinc

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acetate dihydrate and zinc acetate, a blend of zinc oxide and acetic acid. Examples of sodium ion sources are sodium hydroxide and sodium acetate. Sources for the potassium ion include potassium hydroxide and potassium acetate. Suitable nickel ion sources are nickel acetate, nickel oxide and nickel hydroxide. Sources of magnesium include magnesium oxide, magnesium hydroxide, magnesium acetate. Sources of manganese include manganese acetate and manganese oxide.

The new metal cation neutralized high acid ionomer resins are produced by reacting the high acid base copolymer with various amounts of the metal cation salts above the crystalline melting point of the copolymer, such as at a temperature from about 200°F to about 500°F, preferably from about 250°F to about 350°F under high shear conditions at a pressure of from about 10 psi to 10,000 psi. Other well known blending techniques may also be used. The amount of metal cation salt utilized to produce the new metal cation neutralized high acid based ionomer resins is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in the high acid copolymer. The extent of neutralization is generally from about 10% to about 90%.

As indicated below in Table 4 and more specifically in Example 1 in U.S. Application Serial No. Ins a4 08/493,089, a4 a number of new types of metal cation neutralized high acid ionomers can be obtained from the above indicated process. These include new high acid ionomer resins neutralized to various extends with manganese, lithium, potassium, calcium and nickel cations. In addition, when a high acid ethylene/acrylic acid copolymer is utilized as the base copolymer component of the invention and this component is subsequently neutralized to various extents with the metal cation salts producing acrylic acid based high

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acid ionomer resins neutralized with cations such as sodium, potassium, lithium, zinc, magnesium, manganese, calcium and nickel, several new cation neutralized acrylic acid based high acid ionomer resins are produced.

T260X

TABLE 4

Metal Cation Neutralized High Acid Ionomers

Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.	Shore D Hardness
1(NaOH)	6.98	67.5	0.9	.804	71
2(NaOH)	5.66	54.0	2.4	.808	73
3(NaOH)	3.84	35.9	12.2	.812	69
4(NaOH)	2.91	27.0	17.5	.812	(brittle)
5(MnAc)	19.6	71.7	7.5	.809	73
6(MnAc)	23.1	88.3	3.5	.814	77
7(MnAc)	15.3	53.0	7.5	.810	72
8(MnAc)	26.5	106	0.7	.813	(brittle)
9(LiOH)	4.54	71.3	0.6	.810	74
10(LiOH)	3.38	52.5	4.2	.818	72
11(LiOH)	2.34	35.9	18.6	.815	72
12(KOH)	5.30	36.0	19.3	Broke	70
13(KOH)	8.26	57.9	7.18	.804	70
14(KOH)	10.7	77.0	4.3	.801	67
15(ZnAc)	17.9	71.5	0.2	.806	71
16(ZnAc)	13.9	53.0	0.9	.797	69
17(ZnAc)	9.91	36.1	3.4	.793	67
18(MgAc)	17.4	70.7	2.8	.814	74
19(MgAc)	20.6	87.1	1.5	.815	76
20(MgAc)	13.8	53.8	4.1	.814	74
21(CaAc)	13.2	69.2	1.1	.813	74
22(CaAc)	7.12	34.9	10.1	.808	70

Controls: 50/50 Blend of Ioteks 8000/7030 C.O.R.=.810/65 Shore D Hardness

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DuPont High Acid Surlyn® 8422 (Na) C.O.R.=.811/70 Shore D Hardness
DuPont High Acid Surlyn® 8162 (Zn) C.O.R.=.807/65 Shore D Hardness
Exxon High Acid Iotek EX-960 (Zn) C.O.R.=.796/65 Shore D Hardness

TABLE 4 (continued)

Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.
23 (MgO)	2.91	53.5	2.5	.813
24 (MgO)	3.85	71.5	2.8	.808
25 (MgO)	4.76	89.3	1.1	.809
26 (MgO)	1.96	35.7	7.5	.815

Control for Formulations 23-26 is 50/50 Iotek 8000/7030, C.O.R.=.814, Formulation 26 C.O.R. was normalized to that control accordingly

TABLE 4 (continued)

Formulation No.	Wt-% Cation Salt	Wt-% Neutralization	Melt Index	C.O.R.	Shore D Hardness
27 (NiAc)	13.04	61.1	0.2	.802	71
28 (NiAc)	10.71	48.9	0.5	.799	72
29 (NiAc)	8.26	36.7	1.8	.796	69
30 (NiAc)	5.66	24.4	7.5	.786	64

Control for Formulation Nos. 27-30 is 50/50 Iotek 8000/7030, C.O.R.=.807

When compared to low acid versions of similar cation neutralized ionomer resins, the new metal cation neutralized high acid ionomer resins exhibit enhanced hardness, modulus and resilience characteristics. These are properties that are particularly desirable in a number of thermoplastic fields, including the field of golf ball manufacturing.

When utilized in the construction of the inner layer of a multi-layered golf ball, it has been found that the new acrylic acid based high acid ionomers extend the range of hardness beyond that previously obtainable while maintaining the beneficial properties (i.e. durability, click, feel, etc.) of the softer low acid ionomer covered balls, such as balls produced

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utilizing the low acid ionomers disclosed in U.S. Patent Nos. 4,884,814 and 4,911,451.

Moreover, as a result of the development of a number of new acrylic acid based high acid ionomer resins neutralized to various extents by several different types of metal cations, such as manganese, lithium, potassium, calcium and nickel cations, several new ionomers or ionomer blends are now available for production of an inner cover layer of a multi-layered golf ball. By using these high acid ionomer resins, harder, stiffer inner cover layers having higher C.O.R.s, and thus longer distance, can be obtained.

More preferably, it has been found that when two or more of the above-indicated high acid ionomers, particularly blends of sodium and zinc high acid ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further than previously known multi-layered golf balls produced with low acid ionomer resin covers due to the balls' enhanced coefficient of restitution values.

The low acid ionomers which may be suitable for use in formulating the inner layer compositions of several of the embodiments of the subject invention are ionic copolymers which are the metal, i.e., sodium, zinc, magnesium, etc., salts of the reaction product of an olefin having from about 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from about 3 to 8 carbon atoms. Preferably, the ionomeric resins are copolymers of ethylene and either acrylic or methacrylic acid. In some circumstances, an additional comonomer such as an acrylate ester (i.e., iso- or n-butylacrylate, etc.) can also be included to produce a softer terpolymer. The carboxylic acid groups of the copolymer are partially neutralized (i.e., approximately 10-100%, preferably 30 - 70%) by the metal ions. Each of the low acid ionomer resins which may be included in

the inner layer cover compositions of the invention contains 16% by weight of less of a carboxylic acid.

The inner layer compositions include the low acid ionomers such as those developed and sold by E.I. DuPont de Nemours & Company under the trademark "Surlyn®" and by Exxon Corporation under the trademark "Escor®" or tradename "Iotek," or blends thereof.

The low acid ionomer resins available from Exxon under the designation "Escor®" and/or "Iotek," are somewhat similar to the low acid ionomeric resins available under the "Surlyn®" trademark. However, since the Escor®/Iotek ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the "Surlyn®" resins are zinc, sodium, magnesium, etc. salts of poly(ethylene-methacrylic acid), distinct differences in properties exist.

When utilized in the construction of the inner layer of a multi-layered golf ball, it has been found that the low acid ionomer blends extend the range of compression and spin rates beyond that previously obtainable. More preferably, it has been found that when two or more low acid ionomers, particularly blends of sodium and zinc ionomers, are processed to produce the covers of multi-layered golf balls, (i.e., the inner cover layer herein) the resulting golf balls will travel further and at an enhanced spin rate than previously known multi-layered golf balls. Such an improvement is particularly noticeable in enlarged or oversized golf balls.

The use of an inner layer formulated from blends of lower acid ionomers produces multi-layer golf balls having enhanced compression and spin rates. These are the properties desired by the more skilled golfer.

In yet another embodiment of the inner cover layer, a blend of high and low acid ionomer resins is used. These can be the ionomer resins described above, combined in a weight ratio which preferably is within

the range of 10:90 to 90:10 parts of high and low acid ionomer resins.

A further additional embodiment of the inner cover layer is primarily based upon the use of a fully non-ionomeric thermoplastic material. Suitable non-ionomeric materials include metallocene catalyzed polyolefins or polyamides, polyamide/ionomer blends, polyphenylene ether/ionomer blends, etc., which have a shore D hardness of ≥60 and a flex modulus of greater than about 30,000 psi, or other hardness and flex modulus values which are comparable to the properties of the ionomers described above. Other suitable materials include but are not limited to thermoplastic or thermosetting polyurethanes, a polyester elastomer such as that marketed by DuPont under the trademark Hytrel®, or a polyester amide such as that marketed by Elf Atochem S.A. under the trademark Pebax®, a blend of two or more non-ionomeric thermoplastic elastomers, or a blend of one or more ionomers and one or more non-ionomeric thermoplastic elastomers. These materials can be blended with the ionomers described above in order to reduce cost relative to the use of higher quantities of ionomer.

<u>**Outer Cover Layer**</u>

While the dual core component described below, and the hard inner cover layer formed thereon, provide the multi-layer golf ball with power and distance, the outer cover layer 16 is comparatively softer than the inner cover layer. The softness provides for the feel and playability characteristics typically associated with balata or balata-blend balls. The outer cover layer or ply is comprised of a relatively soft, low modulus (about 1,000 psi to about 10,100 psi) and, in an alternate embodiment, low acid (less than 16 weight percent acid) ionomer, an ionomer blend, a non-ionomeric thermoplastic or thermosetting material such as, but not

limited to, a metallocene catalyzed polyolefin such as EXACT material available from EXXON, a polyurethane, a polyester elastomer such as that marketed by DuPont under the trademark Hytrel®, or a polyester amide such as that marketed by Elf Atochem S.A. under the trademark Pebax®, a blend of two or more non-ionomeric thermoplastic or thermosetting materials, or a blend of one or more ionomers and one or more non-ionomeric thermoplastic materials. The outer layer is fairly thin (i.e. from about 0.010 to about 0.10 inches in thickness, more desirably 0.03 to 0.06 inches in thickness for a 1.680 inch ball and 0.04 to 0.07 inches in thickness for a 1.72 inch or more ball), but thick enough to achieve desired playability characteristics while minimizing expense. Thickness is defined as the average thickness of the non-dimpled areas of the outer cover layer. The outer cover layer, such as layer 16, 16 has a Shore D hardness of 55 or less, and more preferably 50 or less.

In one embodiment, the outer cover layer preferably is formed from an ionomer which constitutes at least 75 weight % of an acrylate ester-containing ionic copolymer or blend of acrylate ester-containing ionic copolymers. This type of outer cover layer in combination with the core and inner cover layer described above results in golf ball covers having a favorable combination of durability and spin rate. The one or more acrylate ester-containing ionic copolymers each contain an olefin, an acrylate ester, and an acid. In a blend of two or more acrylate ester-containing ionic copolymers, each copolymer may contain the same or a different olefin, acrylate ester and acid than are contained in the other copolymers. Preferably, the acrylate ester-containing ionic copolymer or copolymers are terpolymers, but additional monomers can be combined into the copolymers if the monomers do not substantially

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reduce the scuff resistance or other good playability properties of the cover.

For a given copolymer, the olefin is selected from the group consisting of olefins having 2 to 8 carbon atoms, including, as non-limiting examples, ethylene, propylene, butene-1, hexene-1 and the like. Preferably the olefin is ethylene.

The acrylate ester is an unsaturated monomer having from 1 to 21 carbon atoms which serves as a softening comonomer. The acrylate ester preferably is methyl, ethyl, n-propyl, n-butyl, n-octyl, 2-ethylhexyl, or 2-methoxyethyl 1-acrylate, and most preferably is methyl acrylate or n-butyl acrylate. Another suitable type of softening comonomer is an alkyl vinyl ether selected from the group consisting of n-butyl, n-hexyl, 2-ethylhexyl, and 2-methoxyethyl vinyl ethers.

The acid is a mono- or dicarboxylic acid and preferably is selected from the group consisting of methacrylic, acrylic, ethacrylic, α-chloroacrylic, crotonic, maleic, fumaric, and itaconic acid, or the like, and half esters of maleic, fumaric and itaconic acid, or the like. The acid group of the copolymer is 10-100% neutralized with any suitable cation, for example, zinc, sodium, magnesium, lithium, potassium, calcium, manganese, nickel, chromium, tin, aluminum, or the like. It has been found that particularly good results are obtained when the neutralization level is about 50-100%.

The one or more acrylate ester-containing ionic copolymers each has an individual Shore D hardness of about 5-64. The overall Shore D hardness of the outer cover is 55 or less, and generally is 40-55. It is preferred that the overall Shore D hardness of the outer cover is in the range of 40-50 in order to impart particularly good playability characteristics to the ball.

The outer cover layer of the invention is formed over a core to result in a golf ball having a coefficient of restitution of at least 0.770, more preferably at least 0.780, and most preferably at least 0.790. The coefficient of restitution of the ball will depend upon the properties of both the core and the cover. The PGA compression of the golf ball is 100 or less, and preferably is 90 or less.

The acrylate ester-containing ionic copolymer or copolymers used in the outer cover layer can be obtained by neutralizing commercially available acrylate ester-containing acid copolymers such as polyethylene-methyl acrylate-acrylic acid terpolymers, including ESCOR ATX (Exxon Chemical Company) or poly (ethylene-butyl acrylate-methacrylic acid) terpolymers, including NUCREL (DuPont Chemical Company). Particularly preferred commercially available materials include ATX 320, ATX 325, ATX 310, ATX 350, and blends of these materials with NUCREL 010 and NUCREL 035. The acid groups of these materials and blends are neutralized with one or more of various cation salts including zinc, sodium, magnesium, lithium, potassium, calcium, manganese, nickel, etc. The degree of neutralization ranges from 10-100%. Generally, a higher degree of neutralization results in a harder and tougher cover material. The properties of non-limiting examples of commercially available un-neutralized acid terpolymers which can be used to form the golf ball outer cover layers of the invention are provided below in Table 5.

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T340X

TABLE 5

Properties of Un-Neutralized Acid Terpolymers

Trade Name	Melt Index dg/min ASTM D 1238	Acid No. % KOH/g	Flex Modulus MPa (ASTM D790)	Hardness (Shore D)
ATX 310	6	45	80	44
ATX 320	5	45	50	34
ATX 325	20	45	9	30
ATX 350	6	15	20	28
Nucrel 010	11	60	40	40
Nucrel 035	35	60	59	40

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a

The ionomer resins used to form the outer cover layers can be produced by reacting the acrylate ester-containing acid copolymer with various amounts of the metal cation salts at a temperature above the crystalline melting point of the copolymer, such as a temperature from about 200°F ~~200/F~~ to about 500°F ~~500/F~~, preferably from about 250°F ~~250/F~~ to about 350°F ~~350/F~~, under high shear conditions at a pressure of from about 100 psi to 10,000 psi. Other well known blending techniques may also be used. The amount of metal cation salt utilized to produce the neutralized ionic copolymers is the quantity which provides a sufficient amount of the metal cations to neutralize the desired percentage of the carboxylic acid groups in the high acid copolymer. When two or more different copolymers are to be used, the copolymers can be blended before or after neutralization. Generally, it is preferable to blend the copolymers before they are neutralized to provide for optimal mixing.

The compatibility of the acrylate ester-containing copolymers with each other in a copolymer blend produces a golf ball outer cover layer having a surprisingly good scuff resistance for a given hardness

of the outer cover layer. The golf ball according to the invention has a scuff resistance of no higher than 3.0. It is preferred that the golf ball has a scuff resistance of no higher than about 2.5 to ensure that the golf ball is scuff resistant when used in conjunction with a variety of types of clubs, including sharp-grooved irons, which are particularly inclined to result in scuffing of golf ball covers. The best results according to the invention are obtained when the outer cover layer has a scuff resistance of no more than about 2.0.

Additional materials may also be added to the inner and outer cover layer of the present invention as long as they do not substantially reduce the playability properties of the ball. Such materials include dyes (for example, Ultramarine Blue sold by Whitaker, Clark, and Daniels of South Plainsfield, N.J.) (see U.S. Pat. No. 4,679,795), pigments such as titanium dioxide, zinc oxide, barium sulfate and zinc sulfate; UV absorbers; antioxidants; antistatic agents; and stabilizers. Moreover, the cover compositions of the present invention may also contain softening agents such as those disclosed in U.S. Patent Nos. 5,312,857 and 5,306,760, including plasticizers, metal stearates, processing acids, etc., and reinforcing materials such as glass fibers and inorganic fillers, as long as the desired properties produced by the golf ball covers of the invention are not impaired.

The outer layer in another embodiment of the invention includes a blend of a soft (low acid) ionomer resin with a small amount of a hard (high acid) ionomer resin. A low modulus ionomer suitable for use in the outer layer blend has a flexural modulus measuring from about 1,000 to about 10,000 psi, with a hardness of about 20 to about 40 on the Shore D scale. A high modulus ionomer herein is one which measures from about 15,000 to about 70,000 psi as measured in accordance

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with ASTM method D-790. The hardness may be defined as at least 50 on the Shore D scale as measured in accordance with ASTM method D-2240.

Soft ionomers primarily are used in formulating the hard/soft blends of the cover compositions. These ionomers include acrylic acid and methacrylic acid based soft ionomers. They are generally characterized as comprising sodium, zinc, or other mono- or divalent metal cation salts of a terpolymer of an olefin having from about 2 to 8 carbon atoms, methacrylic acid, acrylic acid, or another, α, ß-unsaturated carboxylic acid, and an unsaturated monomer of the acrylate ester class having from 1 to 21 carbon atoms. The soft ionomer is preferably made from an acrylic acid base polymer is an unsaturated monomer of the acrylate ester class.

Certain ethylene-acrylic acid based soft ionomer resins developed by the Exxon Corporation under the designation "Iotek 7520" (referred to experimentally by differences in neutralization and melt indexes as LDX 195, LDX 196, LDX 218 and LDX 219) may be combined with known hard ionomers such as those indicated above to produce the inner and outer cover layers. The combination produces higher C.O.R.s at equal or softer hardness, higher melt flow (which corresponds to improved, more efficient molding, i.e., fewer rejects] as well as significant cost savings versus the outer layer of multi-layer balls produced by other known hard-soft ionomer blends as a result of the lower overall raw materials cost and improved yields.

While the exact chemical composition of the resins to be sold by Exxon under the designation Iotek 7520 is considered by Exxon to be confidential and proprietary information, Exxon's experimental product data sheet lists the following physical properties of the ethylene acrylic acid zinc ionomer developed by Exxon:

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T370X

TABLE 6

Physical Properties of Iotek 7520

Property Value	ASTM Method	Units	Typical
Melt Index	D-1238	g/10 min.	2
Density	D-1505	kg/m^3	0.962
Cation			Zinc
Melting Point	D-3417	°C	66
Crystallization Point	D-3417	°C	49
Vicat Softening Point	D-1525	°C	42
Plaque Properties (2 mm thick Compression Molded Plaques)			
Tensile at Break	D-638	MPa	10
Yield Point	D-638	MPa	None
Elongation at Break	D-638	%	760
1% Secant Modulus	D-638	MPa	22
Shore D Hardness	D-2240		32
Flexural Modulus	D-790	MPa	26
Zwick Rebound	ISO 4862	%	52
De Mattia Flex Resistance	D-430	Cycles	>5000

In addition, test data collected by the inventor indicates that Iotek 7520 resins have Short D hardnesses of about 32 to 36 (per ASTM D-2240), melt flow indexes of 3±0.5 g/10 min (at 190/C. per ASTM D-1288), and a flexural modulus of about 2500 - 3500 psi (per ASTM D-790). Furthermore, testing by an independent testing laboratory by pyrolysis mass spectrometry indicates at Iotek 7520 resins are

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generally zinc salts of a terpolymer of ethylene, acrylic acid, and methyl acrylate.

Furthermore, the inventor has found that a newly developed grade of an acrylic acid based soft ionomer available from the Exxon Corporation under the designation Iotek 7510 is also effective when combined with the hard ionomers indicated above in producing golf ball covers exhibiting higher C.O.R. values at equal or softer hardness than those produced by known hard-soft ionomer blends. In this regard, Iotek 7510 has the advantages (i.e. improved flow, higher C.O.R. values at equal hardness, increased clarity, etc.) produced by the Iotek 7520 resin when compared to the methacrylic acid base soft ionomers known in the art (such as the Surlyn® 8625 and Surlyn® 8629 combinations disclosed in U.S. Patent No. 4,8884,814).

In addition, Iotek 7510, when compared to Iotek 7520, produces slightly higher C.O.R. values at equal softness/hardness due to the Iotek 7510's higher hardness and neutralization. Similarly, Iotek 7510 produces better release properties (from the mold cavities) due to its slightly higher stiffness and lower flow rate than Iotek 7520. This is important in production where the soft covered balls tend to have lower yields caused by sticking in the molds and subsequent punched pin marks from the knockouts.

According to Exxon, Iotek 7510 is of similar chemical composition as Iotek 7520 (i.e. a zinc salt of a terpolymer of ethylene, acrylic acid, and methyl acrylate) but is more highly neutralized. Based upon FTIR analysis, Iotek 7520 is estimated to be about 30-40 wt.-% neutralized and Iotek 7510 is estimated to be about 40-60 wt.-% neutralized. The typical properties of Iotek 7510 in comparison of those of Iotek 7520 in comparison of those of Iotek 7520 are set forth below:

T390X

TABLE 7

Physical Properties of Iotek 7510 in Comparison to Iotek 7520

	IOTEK 7520	IOTEK 7510
MI, g/10 min	2.0	0.8
Density, g/cc	0.96	0.97
Melting Point, °F	151	149
Vicat Softening Point, °F	108	109
Flex Modulus, psi	3800	5300
Tensile Strength, psi	1450	1750
Elongation, %	760	690
Hardness, Shore D	32	35

The hard ionomer resins utilized to produce the outer cover layer composition hard/soft blends include ionic copolymers which are the sodium, zinc, magnesium, lithium, etc. salts of the reaction product of an olefin having from 2 to 8 carbon atoms and an unsaturated monocarboxylic acid having from 3 to 8 carbon atoms. The carboxylic acid groups of the copolymer may be totally or partially (i.e. approximately 15-75 percent) neutralized.

The hard ionomeric resins are likely copolymers of ethylene and acrylic and/or methacrylic acid, with copolymers of ethylene and acrylic acid being the most preferred. Two or more types of hard ionomeric resins may be blended into the outer cover layer compositions in order to produce the desired properties of the resulting golf balls.

As discussed earlier herein, the hard ionomeric resins introduced under the designation Escor® and sold under the designation "Iotek" are somewhat similar to the hard ionomeric resins sold under the Surlyn® trademark. However, since the "Iotek" ionomeric resins are sodium or zinc salts of poly(ethylene-acrylic acid) and the Surlyn® resins are zinc or sodium salts of

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poly(ethylene-methacrylic acid) some distinct differences in properties exist. As more specifically indicated in the data set forth below, the hard "Iotek" resins (i.e., the acrylic acid based hard ionomer resins) are the more preferred hard resins for use in formulating the outer layer blends for use in the present invention. In addition, various blends of "Iotek" and Surlyn® hard ionomeric resins, as well as other available ionomeric resins, may be utilized in the present invention in a similar manner.

Examples of commercially available hard ionomeric resins which may be used in the present invention in formulating the outer cover blends include the hard sodium ionic copolymer sold under the trademark Surlyn® 8940 and the hard zinc ionic copolymer sold under the trademark Surlyn® 9910. Surlyn® 8940 is a copolymer of ethylene with methacrylic acid and about 15 weight percent acid which is about 29 percent neutralized with sodium ions. this resin has an average melt flow index of about 2.8. Surlyn® 9910 is a copolymer of ethylene and methacrylic acid with about 15 weight percent acid which is about 58 percent neutralized with zinc ions. The average melt flow index of Surlyn® 9910 is about 0.7. The typical properties of Surlyn® 9910 and 8940 are set forth below in Table 8:

T400X

TABLE 8

Typical Properties of Commercially Available Hard Surlyn® Resins Suitable for Use in the Outer Layer Blends of the Present Invention

	ASTM D	8940	9910	8920	8528	9970	9730
Cation Type		Sodium	Zinc	Sodium	Sodium	Zinc	Zinc
Melt flow index, gms/10 min.	D-1238	2.8	0.7	0.9	1.3	14.0	1.6
Specific Gravity, g/cm³	D-792	0.95	0.97	0.95	0.94	0.95	0.95
Hardness, Shore D	D-2240	66	64	66	60	62	63

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Tensile Strength, (kpsi), MPa	D-638	(4.8) 33.1	(3.6) 24.8	(5.4) 37.2	(4.2) 29.0	(3.2) 22.0	(4.1) 28.0
Elongation, %	D-638	470	290	350	450	460	460
Flexural Modulus, (kpsi) MPa	D-790	(51) 350	(48) 330	(55) 380	(32) 220	(28) 190	(30) 210
Tensile Impact (23°C) KJ/m_2 (ft.-lbs./in^2)	D-1822S	1020 (485)	1020 (485)	865 (410)	1160 (550)	760 (360)	1240 (590)
Vicat Temperature,°C	D-1525	63	62	58	73	61	73

Examples of the more pertinent acrylic acid based hard ionomer resin suitable for use in the present outer cover composition sold under the "Iotek" trade name by the Exxon Corporation include Iotek 8000, 8010, 8020, 8030, 7030, 7010, 7020, 1002, 1003, 959 and 960. The physical properties of Iotek 959 and 960 are shown above. The typical properties of the remainder of these and other Iotek hard ionomers suited for use in formulating the outer layer cover composition are set forth below in Table 9:

TABLE 9

Typical Properties of Iotek Ionomers

T410X

Resin Properties	ASTM Method	Units	4000	4010	8000	8020	8030
Cation type			zinc	zinc	sodium	sodium	sodium
Melt index	D-1238	g/10 min.	2.5	1.5	0.8	1.6	2.8
Density	D-1505	kg/m^3	963	963	954	960	960
Melting Point	D-3417	°C	90	90	90	87.5	87.5
Crystallization Point	D-3417	°C	62	64	56	53	55
Vicat Softening Point	D-1525	°C	62	63	61	64	67
% Weight Acrylic Acid			16		11		
% of Acid Groups cation neutralized			30		40		
Plaque Properties	Method	ASTM Units	4000	4010	8000	8020	8030
(3 mm thick, compression molded)							

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Tensile at break	D-638	MPa	24	26	36	31.5	28
Yield point	D-638	MPa	none	none	21	21	23
Elongation at break	D-638	%	395	420	350	410	395
1% Secant modulus	D-638	MPa	160	160	300	350	390
Shore Hardness D	D-2240	--	55	55	61	58	59

Film Properties (50 micron film 2.2:1 Blow-up ratio)				4000	4010	8000	8020	8030
Tensile at Break	MD	D-882	MPa	41	39	42	52	47.4
	TD	D-882	MPa	37	38	38	38	40.5
Yield point	MD	D-882	MPa	15	17	17	23	21.6
	TD	D-882	MPa	14	15	15	21	20.7
Elongation at Break	MD	D-882	%	310	270	260	295	305
	TD	D-882	%	360	340	280	340	345
1% Secant modulus	MD	D-882	MPa	210	215	390	380	380
	TD	D-882	MPa	200	225	380	350	345
Dart Drop Impact		D-1709	g/micron	12.4	12.5	20.3		

Resin Properties	ASTM Method	Units	7010	7020	7030
Cation type			zinc	zinc	zinc
Melt Index	D-1238	g/10 min.	0.8	1.5	2.5
Density	D-1505	kg/m^3	960	960	960
Melting Point	D-3417	°C	90	90	90
Crystallization Point	D-3417	°C	--	--	--
Vicat Softening Point	D-1525	°C	60	63	62.5
%Weight Acrylic Acid			--	--	--
% of Acid Groups Cation Neutralized			--	--	--

Plaque Properties	ASTM Method	Units	7010	7020	7030
(3 mm thick, compression molded)					
Tensile at break	D-638	MPa	38	38	38
Yield Point	D-638	MPa	none	none	none
Elongation at break	D-638	%	500	420	395
1% Secant modulus	D-638	MPa	--	--	--
Shore Hardness D	D-2240	--	57	55	55

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It has been determined that when hard/soft ionomer blends are used for the outer cover layer, good results are achieved when the relative combination is in a range of about 3-25 percent hard ionomer and about 75-97 percent soft ionomer.

Moreover, in alternative embodiments, the outer cover layer formulation may also comprise up to 100 wt % of a soft, low modulus non-ionomeric thermoplastic material including a polyester polyurethane such as B.F. Goodrich Company's Estane® polyester polyurethane X-4517. The non-ionomeric thermoplastic material may be blended with a soft ionomer. For example, polyamides blend well with soft ionomer. According to B.F. Goodrich, Estane® X-4517 has the following properties:

T430X

Properties of Estane® X-4517

Tensile	1430
100%	815
200%	1024
300%	1193
Elongation	641
Youngs Modulus	1826
Hardness A/D	88/39
Bayshore Rebound	59
Solubility in Water	Insoluble
Melt processing temperature	>350°F (>177°C)
Specific Gravity (H_2O=1)	1.1-1.3

Other soft, relatively low modulus non-ionomeric thermoplastic elastomers may also be utilized to produce the outer cover layer as long as the non-ionomeric thermoplastic elastomers produce the playability and durability characteristics desired without adversely effecting the enhanced travel distance characteristic produced by the high acid ionomer resin composition. These include, but are not limited to thermoplastic polyurethanes such as Texin thermoplastic polyurethanes from Mobay Chemical Co. and the Pellethane

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thermoplastic polyurethanes from Dow Chemical Co.; non-ionomeric thermoset polyurethanes including but not limited to those disclosed in U.S. Patent 5,334,673; cross-linked metallocene catalyzed polyolefins; ionomer/rubber blends such as those in Spalding U.S. Patents 4,986,545; 5,098,105 and 5,187,013; and, Hytrel polyester elastomers from DuPont and Pebax polyesteramides from Elf Atochem S.A.

Dual Core

As noted, the present invention golf balls utilize a unique dual core configuration. Preferably, the cores comprise (i) an interior spherical center component formed from a thermoset material, a thermoplastic material, or combinations thereof and (ii) a core layer disposed about the spherical center component, the core layer formed from a thermoset material, a thermoplastic material, or combinations thereof. Most preferably, the core layer is disposed immediately adjacent to, and in intimate contact with the center component. The cores may further comprise (iii) an optional outer core layer disposed about the core layer. Most preferably, the outer core layer is disposed immediately adjacent to, and in intimate contact with the core layer. The outer core layer may be formed from a thermoset material, a thermoplastic material, or combinations thereof.

The present invention provides several additionally preferred embodiment golf balls utilizing the unique dual core configuration and the previously described cover layers. Referring to FIGURE 3, a preferred embodiment golf ball 35 is illustrated comprising a core 30 formed from a thermoset material surrounded by a core layer 32 formed from a thermoplastic material. A multi-layer cover 34 surrounds the core 30 and core layer 32. The multi-

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layer cover 34 preferably corresponds to the previously described multi-layer cover 12.

As illustrated in FIGURE 4, another preferred embodiment golf ball 45 in accordance with the present invention is illustrated. The preferred embodiment golf ball 45 comprises a core 40 formed from a thermoplastic material surrounded by a core layer 42. The core layer 42 is formed from a thermoset material. A multi-layer cover 44 surrounds the core 40 and the core layer 42. Again, the multi-layer cover 44 preferably corresponds to the previously described multi-layer cover 12.

FIGURE 5 illustrates yet another preferred embodiment golf ball 55 in accordance with the present invention. The preferred embodiment golf ball 55 comprises a core 50 formed from a thermoplastic material. A core layer 52 surrounds the core 50. The core layer 52 is formed from a thermoplastic material which may be the same as the material utilized with the core 50, or one or more other or different thermoplastic materials. The preferred embodiment golf ball 55 utilizes an optional outer core layer 54 that surrounds the core component 50 and the core layer 52. The outer core layer 54 is formed from a thermoplastic material which may be the same or different than any of the thermoplastic materials utilized by the core 50 and the core layer 52. The golf ball 55 further comprises a multi-layer cover 56 that is preferably similar to the previously described multi-layer cover 12.

FIGURE 6 illustrates yet another preferred embodiment golf ball 65 in accordance with the present invention. The preferred embodiment golf ball 65 comprises a core 60 formed from a thermoplastic, thermoset material, or any combination of a thermoset and thermoplastic material. A core layer 62 surrounds the core 60. The core layer 62 is formed from a thermoset material. The preferred embodiment golf ball 65 also comprises an optional outer core layer 64 formed

from a thermoplastic material. A multi-layer cover 66, preferably similar to the previously described multi-layer cover 12, is disposed about, and generally surrounds, the core 60, the core layer 62 and the outer core 64.

A wider array of thermoset materials can be utilized in the present invention dual cores. Examples of suitable thermoset materials include butadiene or any natural or synthetic elastomer, including metallocene polyolefins, polyurethanes, silicones, polyamides, polyureas, or virtually any irreversibly cross-linked resin system. It is also contemplated that epoxy, phenolic, and an array of unsaturated polyester resins could be utilized.

The thermoplastic material utilized in the present invention golf balls and, particularly their dual cores, may be nearly any thermoplastic material. Examples of typical thermoplastic materials for incorporation in the golf balls of the present invention include, but are not limited to, ionomers, polyurethane thermoplastic elastomers, and combinations thereof. It is also contemplated that a wide array of other thermoplastic materials could be utilized, such as polysulfones, fluoropolymers, polyamide-imides, polyarylates, polyaryletherketones, polyaryl sulfones/polyether sulfones, polybenzimidazoles, polyether-imides, polyimides, liquid crystal polymers, polyphenylene sulfides; and specialty high-performance resins, which would include fluoropolymers, polybenzimidazole, and ultrahigh molecular weight polyethylenes.

Additional examples of suitable thermoplastics include metallocenes, polyvinyl chlorides, acrylonitrile-butadiene-styrenes, acrylics, styrene-acrylonitriles, styrene-maleic anhydrides, polyamides (nylons), polycarbonates, polybutylene terephthalates, polyethylene terephthalates, polyphenylene

ethers/polyphenylene oxides, reinforced polypropylenes, and high-impact polystyrenes.

Preferably, the thermoplastic materials have relatively high melting points, such as a melting point of at least about 300°F. Several examples of these preferred thermoplastic materials and which are commercially available include, but are not limited to, Capron (a blend of nylon and ionomer), Lexan polycarbonate, Pebax, and Hytrel. The polymers or resin system may be cross-linked by a variety of means such as by peroxide agents, sulphur agents, radiation or other cross-linking techniques.

Any or all of the previously described components in the cores of the golf ball of the present invention may be formed in such a manner, or have suitable fillers added, so that their resulting density is decreased or increased. For example, any of these components in the dual cores could be formed or otherwise produced to be light in weight. For instance, the components could be foamed, either separately or in-situ. Related to this, a foamed light weight filler agent may be added. In contrast, any of these components could be mixed with or otherwise receive various high density filler agents or other weighting components such as relatively high density fibers or particulate agents in order to increase their mass or weight.

The following commercially available thermoplastic resins are particularly preferred for use in the noted dual cores employed in the golf balls of the present invention: Capron 8351 (available from Allied Signal Plastics), Lexan ML5776 (from General Electric), Pebax 3533 (a polyether block amide from Elf Atochem), and Hytrel G4074 (from DuPont). Properties of these four preferred thermoplastics are set forth below in Tables 10-13. When forming a golf ball in accordance with the present invention, if the interior center

component of the dual core is to comprise a thermoplastic material, it is most preferred to utilize Pebax thermoplastic resin.

T480X

TABLE 10

CAPRON 8351

	DAM	50%RH	ASTM Test
MECHANICAL			
Tensile Strength, Yield, psi (MPa)	7,800 (54)	--	D-638
Flexural Strength, psi (MPa)	9,500 (65)	--	D-790
Flexural Modulus, psi (MPa)	230,000 (1,585)	--	D-790
Ultimate Elongation, %	200	--	D-638
Notched Izod Impact, ft-lbs/in (J/M)	No Break	--	D-256
Drop Weight Impact, ft-lbs (J)	150 (200)	--	D-3029
Drop Weight Impact, @ -40°F, ft-lbs (J)	150 (200)	--	D-3029
PHYSICAL			
Specific Gravity	1.07	--	D-792
THERMAL			
Melting Point, °F (°C)	420 (215)	--	D-789
Heat Deflection @ 264 psi °F (°C)	140 (60)	--	D-648

T481X

TABLE 11

Lexan ML5776

PROPERTY	TYPICAL DATA	UNIT	METHOD
MECHANICAL			
Tensile Strength, yield, Type I, 0.125"	8500	psi	ASTM D 638
Tensile Strength, break, Type I, 0.125"	9500	psi	ASTM D 638
Tensile Elongation, yield, Type I, 0.125"	110.0	%	ASTM D 638
Flexural Strength, yield, 0.125"	12000	psi	ASTM D 790
Flexural Modulus, 0.125"	310000	psi	ASTM D 790
IMPACT			

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Izod Impact, unnotched, 73F	60.0	ft-lb/in	ASTM D 4812
Izod Impact, notched, 73F	15.5	ft-lb/in	ASTM D 256
Izod Impact, notches 73F, 0.250"	12.0	ft-lb/in	ASTM D 256
Instrumented Impact Energy @ Peak, 73F	48.0	ft-lbs	ASTM D 3763
THERMAL			
HDT, 264 psi, 0.250", unannealed	257	deg F	ASTM D 648
Thermal Index, Elec Prop	80	deg C	UL 7468
Thermal Index, Mech Prop with Impact	80	deg C	UL 7468
Thermal Index, Mech Prop without Impact	80	deg C	UL 7468
PHYSICAL			
Specific Gravity, solid	1.19	-	ASTM D 792
Water Absorption, 24 hours @ 73F	0.150	%	ASTM D 570
Mold Shrinkage, flow, 0.125"	5.7	in/in E-3	ASTM D 955
Melt Flow Rate, nom'l, 300C/1.2kgf(0)	7.5	g/10 min	ASTM D 1238
FLAME CHARACTERISTICS			
UL File Number, USA	E121562	-	-
94HB Rated (tested thickness)	0.060	inch	UL94

TABLE 12

PEBAX® RESINS

T490X

PROPERTY	ASTM TEST METHOD	UNITS	3533
Specific Gravity	D792		
Water Absorption Equilibrium (20°C, 50% R.H.>)			0.5
24 Hr. Immersion	D570		1.2
Hardness	D2240		35D
Tensile Strength, Ultimate	D638	psi	5600
Elongation, Ultimate	D638	%	580
Flexural Modulus	D790	psi	2800
Izod Impact, Notched	D256	ft-lb./in.	
20°C			NB
-40°C			NB
Abrasion Resistance H18/1000g	D1044	Mg/1000 Cycles	104

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Tear Resistance Notched	D624C	lb./in.	260
Melting Point	D3418	°F	306
Vicat Softening Point	D1525	°F	165
HDT 66 psi	D648	°F	115
Compression Set (24 hr., 160°F)	D395A	%	54

T500X

TABLE 13

HYTREL G4074

Thermoplastic Elastomer

PHYSICAL			
Dens/Sp Gr	ASTM D792	1.1800	sp gr 23/23C
Melt Flow	ASTM D1238	5.20 @E - 190 C/2.16 kg	g/10/min
Wat Abs	ASTM D570	2.100 %	
MECHANICAL			
Elong@Brk	ASTM D638	230.0%	
Flex Mod	ASTM D790	9500psi	
TnStr@Brk	ASTM D638	2000psi	
IMPACT			
Notch Izod	ASTM D256	No Break @ 73.0 F	@0.2500 inft-lb/in
		0.50 @ -40.0 F	@0.2500 inft-lb/in
HARDNESS			
Shore	ASTM D2240	40 Shore D	
THERMAL			
DTUL@66	ASTM D648	122 F	
Melt Point		338.0 F	
Vicat Soft Melt Point	ASTM D1525	248 F	

The cores of the inventive golf balls typically have a coefficient of restitution of about 0.750 or more, more preferably 0.770 or more and a PGA compression of about 90 or less, and more preferably 70

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or less. The cores have a weight of 25 -40 grams and preferably 30 - 40 grams. The core can be compression molded from a slug of uncured or lightly cured elastomer composition comprising a high cis content polybutadiene and a metal salt of an α, β, ethylenically unsaturated carboxylic acid such as zinc mono- or diacrylate or methacrylate. to achieve higher coefficients of restitution and/or to increase hardness in the core, the manufacturer may include a small amount of a metal oxide such as zinc oxide. In addition, larger amounts of metal oxide than are needed to achieve the desired coefficient may be included in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 ounces. Non-limiting examples of other materials which may be used in the core composition including compatible rubbers or ionomers, and low molecular weight fatty acids such as stearic acid. Free radical initiator catalysts such as peroxides are admixed with the core composition so that on the application of heat and pressure, a curing or cross-linking reaction takes place.

Wound cores are generally produced by winding a very long elastic thread around a solid or liquid filled balloon center. The elastic thread is wound around the center to produce a finished core of about 1.4 to 1.6 inches in diameter, generally. However, the preferred embodiment golf balls of the present invention preferably utilize a solid core, or rather a solid dual core configuration, as opposed to a wound core.

Method of Making Golf Ball

In preparing golf balls in accordance with the present invention, a hard inner cover layer is molded (by injection molding or by compression molding) about a core (preferably a solid core, and most preferably a

dual core). A comparatively softer outer layer is molded over the inner layer.

The dual cores of the present invention are preferably formed by compression molding techniques. However, it is fully contemplated that liquid injection molding or transfer molding techniques could be utilized.

For purposes of example, a preferred method of making the golf ball 45 depicted in FIGURE 4 is as follows. Specifically, a thermoset material, i.e. a core layer 42, is formed about an inner core component 40 comprising a thermoplastic material as follows: Referring to FIGURE 7, preforms 75 of a thermoset material, i.e. utilized to form the core layer 42, are preheated in an oven for one-half hour at 170°F and placed in the bottom 73 of a molding assembly 70. A Teflon-coated plate 76 with two hemispheres 77 and 78, each about 0.840 inches in diameter, is placed on top of the preforms. Additional preforms, preheated as described above, are placed in the corresponding cavities of a top mold 72. The bottom mold 73 is engaged with the top mold 72 and the assembly flipped or otherwise inverted. The bottom one half of the mold assembly 70 then becomes the top one half of the mold assembly. The mold assembly 70 is then placed in a press and cold formed at room temperature using approximately 10 tons of pressure in a steam press. The molding assembly 70 is closed for approximately two minutes and pressure released. The molding assembly 70 is then opened and the Teflon plate 76 is removed thereby leaving one or more essentially perfectly formed one-half shells in cavities in the thermoset material. Previously formed thermoplastic core centers are then placed in the bottom cavities and the top portion 72 of the molding assembly 70 is placed on the bottom 73 and the materials disposed therebetween cured. The golf ball produced by this method had an inner core diameter

of 0.840 inches in diameter. The outer core diameter had a final diameter of 1.470 inches, and a pre-mold diameter of 1.490 inches. A relatively hard inner cover layer is then molded about the resulting dual core component. The diameter of the inner cover was 1.570 inches. A comparatively softer outer cover layer is then molded about the inner cover layer. The outer cover diameter was 1.680 inches. Details of molding the inner and outer covers are set forth below.

Four golf balls in accordance with the present invention were formed, each using a preferred and commercially available high melting point thermoplastic material as an inner core component. Table 14, set forth below, summarizes these balls.

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T540X

TABLE 14

		Capron 8351	Lexan ML 5776-7539	Pebax 3533	Hytrel G-4074	Control (Single Core)
Inner Core	size (inches)	0.835	0.854	0.840	0.831	--
	weight (grams)	5.33	6.14	5.08	5.81	--
	rebound %(100")	78	83	65	61	--
	Shore C (surface)	--	--	57	73	--
	Shore D (surface)	75	83	36	47	--
Outer Core Formulation	Cis 1,4 Polybutadiene	100	100	100	100	100
	Zinc oxide	27	26	28	21	25
	Zinc stearate	16	16	16	16	25
	Zinc diacrylate	20	20	24	24	18
	231 x L	0.9	0.9	0.9	0.9	0.9
		163.9	162.9	168.9	161.9	158.9
Double Core Properties	size (inches)	1.561	1.560	1.562	1.563	1.562
	weight (grams)	37.7	37.8	37.8	37.5	37.8
	compression (riehle)	79	80	99	93	114
	COR	.689	.603	.756	.729	.761
Molded Ball Properties	size (inches	1.685	1.683	1.682	1.683	1.685
	weight (grams)	45.3	45.5	45.5	45.2	45.4
	compression (riehle)	78	80	89	87	102
	COR	.750	.667	.785	.761	.788

Cover Stock (used on all above balls)	surlyn 8940	22	*T.G. MB	Iotek 7030	75.35
	surlyn 9910	54.5		Unitane 0-110	23.9
	surlyn 8320	10		Ultra Marine Blue	0.46
	surlyn 8120	4		Eastonbrite OB-1	
	T.B. MB*	9.5		Santonox R	0.038
		100.0			100.00

Generally, the inner cover layer which is molded over the core, or preferably a dual core component, is about 0.01 inches to about 0.10 inches in thickness, preferably about 0.03-0.07 inches thick. The inner ball which includes the core and inner cover layer preferably has a diameter in the range of 1.25 to 1.60 inches. The outer cover layer is about 0.01 inches to about 0.10 inches in thickness. Together, the core, the inner cover layer and the outer cover layer combine to form a ball having a diameter of 1.680 inches or more, the minimum diameter permitted by the rules of the United States Golf Association and weighing no more than 1.62 ounces.

Most preferably, the resulting golf balls in accordance with the present invention have the following dimensions:

Size Specifications:		Preferred	Most Preferred
Inner Core	- Max.	1.250"	1.00"
	- Min.	0.500"	0.70"
Outer Core	- Max.	1.600"	1.570"
	- Min.	1.500"	1.550"
(1) Cover Thickness (Total)			
	- Max.	0.090"	0.065"
	- Min.	0.040"	0.055"

T550X

In a particularly preferred embodiment of the invention, the golf ball has a dimple pattern which provides coverage of 65% or more. The golf ball typically is coated with a durable, abrasion-resistant, relatively non-yellowing finish coat.

The various cover composition layers of the present invention may be produced according to

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conventional melt blending procedures. Generally, the copolymer resins are blended in a Banbury type mixer, two-roll mill, or extruder prior to neutralization. After blending, neutralization then occurs in the melt or molten states in the banbury mixer. Mixing problems are minimal because preferably more than 75 wt %, and more preferably at least 80 wt % of the ionic copolymers in the mixture contain acrylate esters and, in this respect, most of the polymer chains in the mixture are similar to each other. The blended composition is then formed into slabs, pellets, etc., and maintained in such a state until molding is desired. Alternatively, a simple dry blend of the pelletized or granulated resins which have previously been neutralized to a desired extent and colored masterbatch may be prepared and fed directly into the injection molding machine where homogenization occurs in the mixing section of the barrel prior to injection into the mold. If necessary, further additives such as an inorganic filler, etc., may be added and uniformly mixed before initiation of the molding process. A similar process is utilized to formulate the high acid ionomer resin compositions used to produce the inner cover layer. In one embodiment of the invention, a masterbatch of non-acrylate ester-containing ionomer with pigments and other additives incorporated therein is mixed with the acrylate ester-containing copolymers in a ratio of about 1 - 7 weight % masterbatch and 93 - 99 weight % acrylate ester-containing copolymer.

The golf balls of the present invention can be produced by molding processes which include but are not limited to those which are currently well known in the golf ball art. For example, the golf balls can be produced by injection molding or compression molding the novel cover compositions around a wound or solid molded core to produce an inner ball which typically has a diameter of about 1.50 to 1.67 inches. The core, preferably of a dual core configuration, may be formed as

previously described. The outer layer is subsequently molded over the inner layer to produce a golf ball having a diameter of 1.620 inches or more, preferably about 1.680 inches or more. Although either solid cores or wound cores can be used in the present invention, as a result of their lower cost and superior performance solid molded cores are preferred over wound cores. The standards for both the minimum diameter and maximum weight of the balls are established by the United States Golf Association (U.S.G.A.).

In compression molding, the inner cover composition is formed via injection at about 380°F to about 450°F into smooth surfaced hemispherical shells which are then positioned around the core in a mold having the desired inner cover thickness and subjected to compression molding at 200° to 300°F for about 2 to 10 minutes, followed by cooling at 50° to 70°F for about 2 to 7 minutes to fuse the shells together to form a unitary intermediate ball. In addition, the intermediate balls may be produced by injection molding wherein the inner cover layer is injected directly around the core placed at the center of an intermediate ball mold for a period of time in a mold temperature of from 50° to about 100°F. Subsequently, the outer cover layer is molded around the core and the inner layer by similar compression or injection molding techniques to form a dimpled golf ball of a diameter of 1.680 inches or more.

After molding, the golf balls produced may undergo various further processing steps such as buffing, painting and marking as disclosed in U.S. Patent No. 4,911,451.

The resulting golf ball produced from the hard inner layer and the relatively softer, low flexural modulus outer layer provide for an improved multi-layer golf ball having a unique dual core configuration which provides for desirable coefficient of restitution and durability properties while at the same time offering the

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feel and spin characteristics associated with soft balata and balata-like covers of the prior art.

The invention has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon a reading and understanding the preceding detailed description. It is intended that the invention be construed as including all such modifications and alterations in so far as they come within the scope of the appended claims or the equivalents thereof.